CZTS thin films for photovoltaic buildings: *ab initio* thermodynamics

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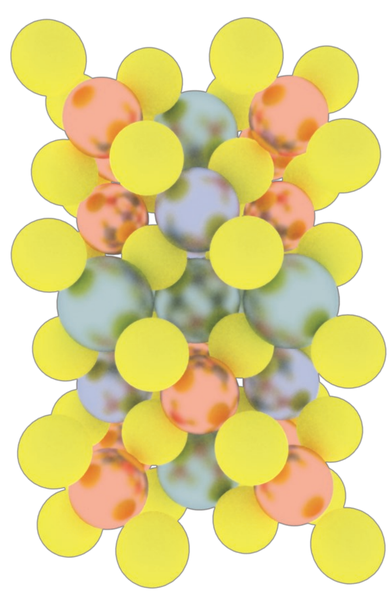
Thin-film inorganic photovoltaics

The field of photovoltaics (PV) is extremely active, with research progressing rapidly in silicon, organic, inorganic, dye-sensitized and hybrid technologies. Thin-film PV uses inorganic compounds with direct bandgaps and high absorption coefficients for the absorber layer in a (typically) single-junction device. These layers are typically polycrystalline and very thin (1-2μm). Ideal materials have a bandgap of 1.1-1.5eV, enabling the optimal Shockly-Quisser efficiency limit of around 30% efficiency for a single-junction device. Already, copper indium gallium selenide (CIGS) cells have achieved laboratory efficiencies of ~20% and commercial efficiencies of ~15%. Cadmium telluride cells have slightly lower efficiencies but a substantial manufacturing base, and together CIGS and CdTe are giving us an explosion in low-cost, lightweight, flexible PV cells.

However, providing PV energy on the scale that it is truly needed will require something more ambitious, on the scale of square kilometers rather than square meters. At this level, supply issues are likely to set in for the rare elements In, Ga, Cd and Te. Copper zinc tin sulfide/selenide (CZTS) looks set to take over as supply stresses set in; record efficiencies are not far behind, having just broken the 10% threshold.

Cu_2ZnSnS_4: CZTS



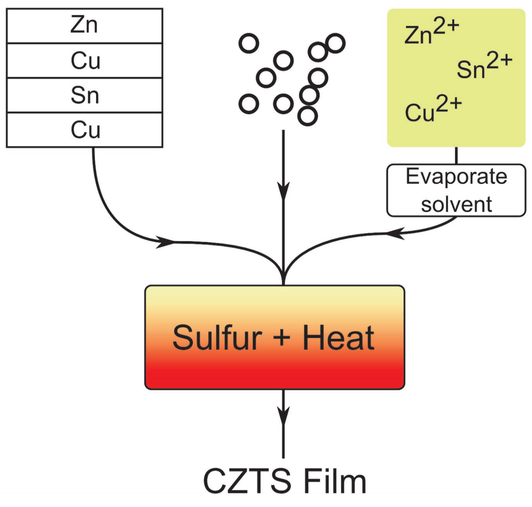
Unit cell of kesterite CZTS. Yellow atoms represent S, pink atoms Cu, green Sn and purple Zn.

CZTS fulfils the requirements for an effective thin-film PV absorber, with a direct bandgap of around 1.5 eV. It is isoelectronic to the simpler II-VI semiconductors such as ZnS; substituting Zn (group II) for a mixture of Cu (group I) and In/Ga (group III) gives CIGS; further substituting the In and Ga with a mixture of Zn (group II) and Sn (group IV) yields the isoelectronic I_2-II-IV-VI_4 compound.

ZnS II-VI → CIGS I-III-VI_2 → CZTS I_2-II-IV-VI_4

The great challenge in working with CZTS lies in controlling the phase equilibrium. As well as a number of possible CZTS phases (dominated by the minimum-energy kesterite phase), relatively small imbalances in the stoichiometry permit the existence of ZnS, Cu_2S, several ternary phases and even liquid tin (at elevated temperatures).

Roll-to-roll processing



Precursors to film formation include electrochemically prepared metal/alloy stacks, precipitated CZTS nanocrystals and/or salt solutions in solvents; in all cases this is followed by annealing with a source of sulphur/selenium.

Large-scale production of thin-film devices is a significant scale-up problem. While there is some interest in flexible polymeric substrates, building-sized devices need to be supported on more traditional engineering materials.

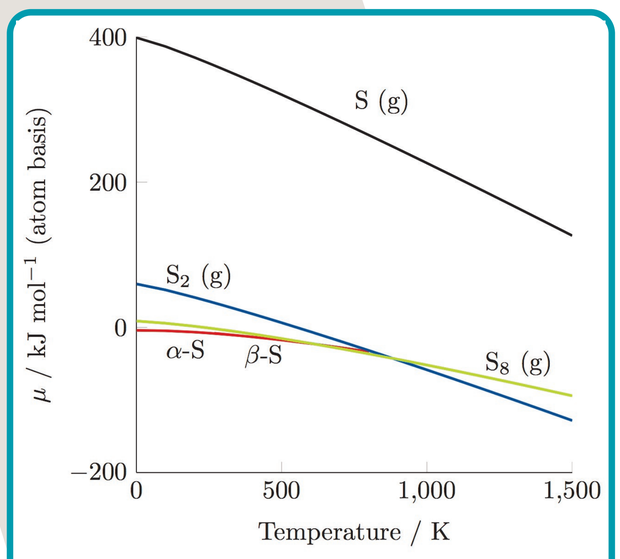
SPECIFIC is a collaboration between academic and industrial groups including Tata Steel and NSG Pilkington. They are developing a range of roll-to-roll processes for functional coatings on steel and glass sheets—these may then be used as cladding for buildings.

CZTS and related materials are seen as strong candidates for photovoltaic coatings in the long term, helping to achieve their vision of "buildings as power plants". Plausible unit operations include spray and inkjet deposition, near-infrared (NIR) heating and screen printing.

Thermochemistry of Sulfur

One of the most appealing aspects of chalcogenide semiconductors is that simple elemental sulfur may be used as a reagent. Sulfur is highly abundant, stable and relatively non-toxic. Although it is used in great quantities in the production of sulphuric acid, it is not generally seen as a "mainstream" reagent and a difficult synthesis is more likely to use reactive (and toxic) H_2S gas.

There are relatively few experimental studies into the thermochemistry of sulfur, and the standard data for most of the gas phases is based on IR spectroscopy and assuming the ideal gas law. A mixture of cyclic allotropes is present in the vapour phase.



Chemical potential of sulphur phases at 1 bar pressure from reference data

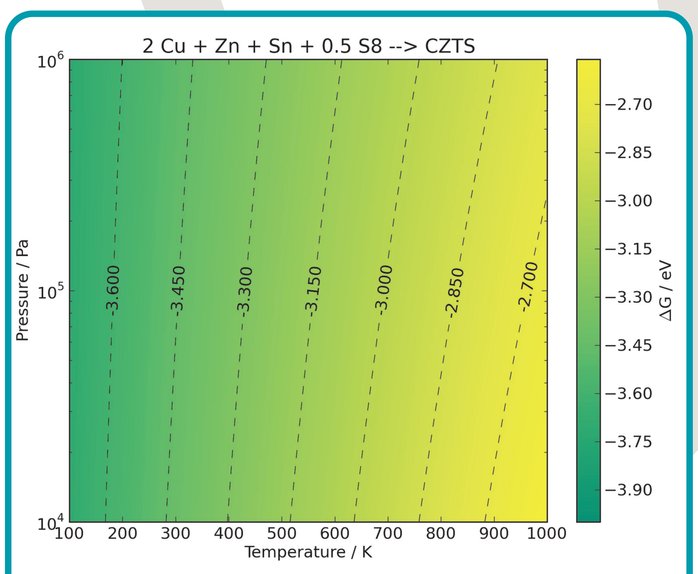
Ab initio thermodynamics

Thermodynamics is an essential tool for the prediction and understanding of phase equilibria, reaction energies and spontaneity. Of particular interest in chemistry is the Gibbs free energy *G*, which for a multicomponent system is approximately the sum of the chemical potentials μ of its components. In order to probe a range of reaction conditions, we need temperature and pressure -dependent chemical potentials for all the reaction components *i*. Disregarding any nuclear effects, these can be related to the electrostatic potential and vibrational energies:

$$\mu_i(T,P) = E_{\mathrm{pot}} + E_{\mathrm{vib}} + \int\int \mu_i \mathrm{d}P\mathrm{d}T = E_{\mathrm{pot}} + E_{\mathrm{ZPE}} + \int C_p \mathrm{d}T + \int V \mathrm{d}P + \int S \mathrm{d}T$$

Energies are calculated with density functional theory (DFT) calculations. Vibrational properties may be available from experimental data, or can also be computed with DFT. Combining μ to obtain ΔG, we can assess the viability of a reaction and equilibria of competing reactions.

The preferred *ab initio* code for this project is FHI-aims, a modern package capable of scaling across thousands of cores. This has allowed us to make use of national-scale computing resources HECToR and Blue Joule, with large calculations using over 4,000 cores. The PBEsol functional is preferred; this is a relatively universal functional with a good balance of cost and accuracy for solid -state systems. The Phonopy package is used for lattice dynamics and hence heat capacity and IR absorption models. For modeling electronic properties including optical absorption spectra, more advanced electronic structure methods are called for: GW, or hybrid functionals such as B3LYP.



Computed free energy surface for the formation of CZTS from S8 vapour. The negative ΔG values show this is favourable across the modelled range of conditions.

Current work and goals

Model development: Ground-state energies and vibrational frequencies within the harmonic approximation have been found for kesterite CZTS, the metals and α-sulfur. Modern programming tools allow for powerful and spontaneous analysis of research data. Dispersion-corrected functionals may give improved values; as well as pair interactions, a multi-body approach has recently become available.

Beyond the harmonic approximation: The quasi-harmonic approximation, electronic thermodynamic integration and molecular dynamics simulations offer increasingly accurate properties at increasing cost.

NIR absorption: absorption spectra from lattice dynamics calculations can be used to predict the mode of NIR heating for a layered structure, informing process design.

H_2S vs S vs SnS: A range of sulfur sources are available and in use. By mapping out the chemical potentials with respect to CZTS and defect formation, we can find out what kind of processing conditions best suit each option - and hence which option best suits our conditions.

Acknowledgements Large calculations have been carried out using:

HECToR, the UK national academic supercomputer, courtesy of our membership of the Materials Chemistry Consortium (funded by the EPSRC);

Blue Joule, the UK 's most powerful supercomputer, courtesy of the Science and Technology Facilities Council (STFC) as part of the early access programme;

Aquila, the University of Bath cluster managed by BUCS.